TRANSLATION

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(54) [Title of/Invention]: **WORKING MEDIUM MIXTURES**

(57) [Claims]

[Claim 1]

A working medium mixture comprising, as essential ingredients thereof, at least one selected from n-butane, isobutane, cyclobutane, n-pentane, isopentane, and cyclopentane, and tetrafluoroethane.

[Detailed Description of the Invention]

[Use of Industrial Utility]

The present invention relates to a novel working medium mixture that can be used in refrigerators, heat pumps, and the like.

Air conditioners, freezers and refrigerators (refrigeration cycles and heat pump cycles), waste heat recovery-power generators (Rankin cycle), heat exchangers (heat pipes), and the like, have been commercialized or test developed. Known working media used in these machines include water and hydrocarbons such as propane, butane, and the like, fluorinated hydrocarbons such as trichlorofluoromethane (R11), chlorodifluoromethane (R22), ammonia, and the like.

[Problem to be Solved by the Invention]

Since fluorinated hydrocarbons are minimally toxic, non-flammable, and chemically stable and a variety of fluorinate hydrocarbons with different standard boiling points are readily available, there are active ongoing studies to evaluate these as working media. The present invention relates to novel fluorinated hydrocarbons that are highly efficient for heat recovery, in particular, efficient in freezers, refrigerators, air conditioners, hot water supply units, or heat pumps aimed at waste heat recovery.

[Means Used to Solve the Problem]

The present invention is a working medium mixture comprising, as essential ingredients thereof, at least one selected from n-butane, isobutane, cyclobutane, n-pentane, isopentane, and cyclopentane and tetrafluoroethane.

The tetrafluoroethane used in this invention is known to have two isomers, 1,1,2,2-tetrafluoroethane (R134) and 1,1,1,2-tetrafluoroethane (R134a) which can be used individually or as a mixture because their physical properties are similar to each other. The present invention is now specifically explained with reference to Figure 1 that shows a flow sheet for a refrigeration cycle using a working medium mixture of this invention (hereafter sometimes referred to as "working medium"). Figure 1 shows 1: a compressor; 2: a condenser; 3 and 3': pipes for load fluid; 4: a pressure reducer; 5: a vaporizer; 6, 6': heat source fluid pipes.

In the refrigeration cycle shown in Figure 1, the working medium is compressed by the compressor 1, led to condenser 2, cooled by a load fluid introduced from pipe 3, and condensed in said condenser 2. The load fluid is, on the other hand, heated in the condenser 2 to be sent via pipe 3' for heating the load. Then, the condensed working medium is reduced in pressure by the pressure reducer 4, led to vaporizer 5, heated by the heat source

fluid that is introduced from pipe 6 in said vaporizer 5 and exits from pipe 6', and then is pulled again into the compressor 1, thereby repeating the above cycle. On the other hand, the heat medium is, in contrast, cooled in the vaporizer 5 and submitted to cooling via pipe 6'. Figures 2 and 3 show the cycles of the working medium mixture in the refrigeration cycle system illustrated in Figure 1 filled in on pressure-enthalpy diagrams. Figure 2 shows a working medium which assumes a wet[liquefied] state when its saturated vapor is adiabatically compressed, whereas Figure 3 shows a counterpart assuming a dry state therein.

The change in the working medium effected by the compressor shown in Figure 1 corresponds to a change in Sign **8** to **9** or **13** to **14** in Figures 2 and 3; the change in the working medium effected by the condenser corresponds to **9→10→11** or **14→15→16→17**; the change in the working medium effected by the pressure reducer corresponds to a change from **11** to **12** or **17** to **18**; the change in the working medium effected by the vaporizer corresponds to a change from **8** or **18** to **13**, respectively.

The operating conditions for the refrigeration cycle system of Figure 1 using the working medium mixture of this invention were set in terms of the temperature at which vaporization ceases (temperature at sign 7 or 13, hereafter vaporization temperature) of the working medium in the evaporator; the temperature at which condensation commences for the working medium in the condenser (temperature at Sign **9** or **15**, hereafter condensation temperature). Tables 1 to 12 show the performance coefficient according to the above freezing cycle system using the working medium mixtures of this invention and the cooling capacity per compressor unit volume, along with comparative examples. As can be grasped from the Tables, the working medium mixtures of the present invention consisting of essential components of a hydrocarbon containing 4-5 carbon atoms, one selected from n-butane, isobutane, cyclobutane, n-pentane, isopentane, and cyclopentane, and R134a, can provide substantial improvements over the case where n-butane, isobutane, cyclobutane, n-pentane, isopentane, and cyclopentane, or R134a are used individually; in particular, a much greater improvement is achieved by working medium mixtures containing about 20 mole % of R134a over the use of n-butane, isobutane, cyclobutane, n-pentane, isopentane, and cyclopentane, or R134a alone. A hydrocarbon containing 4-5 carbon atoms, one of the components in the working medium mixtures of this invention, shows higher performance coefficients compared to R134a, but it is deficient: i.e. lower

refrigeration capacities per compressor unit volume and flammability. On the other hand, while R134a is deficiently lower in performance coefficient compared to hydrocarbons with 4-5 carbon atoms, it has the advantages of high refrigeration capacity per compressor unit volume and being non-flammable . Accordingly it is noted that use of the working medium mixture of this invention is extremely effective in that it can improve on individual component's shortcomings while making use of the above advantages. The working medium mixtures of the present invention are particularly effective for application to refrigeration cycles aimed at low to high temperature air conditioning, freezing, and refrigeration, but they can also be used as working media in Rankin cycles or other heat recovery technologies. The working medium mixture of this invention is highly heat stable requiring no stabilizers under the usual service conditions, but if it is necessary to upgrade heat stability for severe use conditions, one may add a small amount, about 1 part by weight of a stabilizer to 100 parts by weight of working medium, a stabilizer like a phosphite compound such as dimethyl phosphite, diisopropyl phosphite, diphenyl phosphite, and the like, a thiophosphite or phosphine sulfide compound such as triphenyl phosphine sulfide, trimethyl phosphine sulfide, and a glycidyl ether, and the like.

It is anticipated that tetrafluoroethane is poorly compatible with the lubricating oils that are used in refrigerators, heat pumps, and the like, but one component of the working medium mixture composition of this invention is a hydrocarbon which is highly compatible with lubricating oil. That is, the working media mixture of this invention are expected to improve over the single use of tetrafluoroethane in compatibility toward lubricating oils.

Table 1 (Vaporization Temperature: 0°C, Condensation Temperature: 60°C, Degree of Supercooling: 0°C

R134a/n-butane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.04	3.08	3.14	3.21	3.36	3.51	3.40
Refrigeration Capacity (kcal/m^3)	370	355	330	305	250	195	160

Table 2 (Vaporization Temperature: -20°C, Condensation Temperature: 40°C, Degree of Super Cooling: 0°C)

R134a/n-butane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.07	3.10	3.14	3.17	3.26	3.37	3.26
Refrigeration Capacity	210	200	180	165	130	100	80

(kcal/m³)							

Table 3 (Vaporization Temperature: 0°C, Condensation Temperature: 60°C, Degree of Super Cooling: 0°C)

R134a/isobutane molar ratio	100/90	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.04	3.04	3.04	3.08	3.18	3.31	3.26
Refrigeration Capacity (kcal/m³)	370	365	355	345	310	250	215

Table 4 (Vaporization Temperature: -20°C, Condensation Temperature: 40°C, Degree of Super Cooling: 0°C)

R134a/isobutane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.07	3.07	3.07	3.09	3.15	3.22	3.16
Refrigeration Capacity (kcal/m³)	210	205	200	195	170	140	115

Table 5 (Vaporization Temperature: 0°C, Condensation Temperature: 60°C, Degree of Super Cooling: 0°C)

R134a/cyclobutane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.04	3.16	3.27	3.39	3.63	3.86	3.71
Refrigeration Capacity (kcal/m³)	370	335	290	255	200	150	120

Table 6 (Vaporization Temperature: -20°C, Condensation Temperature: 40°C, Degree of Super Cooling: 0°C)

R134a/cyclobutane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.07	3.14	3.20	3.28	3.46	3.63	3.53
Refrigeration Capacity (kcal/m³)	210	180	150	125	95	70	55

Table 7 (Vaporization Temperature: 0°C, Condensation Temperature: 60°C, Degree of Super Cooling: 0°C)

R134a/n-pentane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	2/100
Performance Coefficient (-)	3.04	3.04	3.23	3.47	3.89	4.14	3.55

Refrigeration Capacity ($kcal/m^3$)	370	245	175	140	100	70	50

Table 8 (Vaporization Temperature: -20°C, Condensation Temperature: 40°C, Degree of Super Cooling: 0°C)

R134a/n-pentane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.07	3.11	3.31	3.63	3.86	3.75	3.34
Refrigeration Capacity ($kcal/m^3$)	210	80	60	40	30	25	20

Table 9 (Vaporization Temperature: 0°C, Condensation Temperature: 60°C, Degree of Super Cooling: 0°C)

R134a/isopentane molar ratio	100/0	90/10	80/20	70/30	50/50	20/80	0/100
Performance Coefficient (-)	3.04	3.08	3.18	3.39	3.78	4.04	3.52
Refrigeration Capacity ($kcal/m^3$)	370	290	215	175	130	90	65

Table 10 (Vaporization Temperature: -20°C, Condensation Temperature: 40°C, Degree of Super Cooling: 0°C)

R134a/isopentane-butan molar ratio	100/0	80/20	70/30	50/50	20/80	10/90	0/100
Performance Coefficient (-)	3.07	3.10	3.25	3.55	3.78	3.68	3.31
Refrigeration Capacity ($kcal/m^3$)	210	105	80	60	40	35	30

Table 11 (Vaporization Temperature: 0°C, Condensation Temperature: 60°C, Degree of Super Cooling: 0°C)

R134a/cyclopentane molar ratio	100/0	80/20	70/30	50/50	20/80	10/90	0/100
Performance Coefficient (-)	3.04	3.28	3.84	4.24	4.46	4.39	3.83
Refrigeration Capacity ($kcal/m^3$)	370	130	80	60	50	45	35

Table 12 (Vaporization Temperature: -20°C, Condensation Temperature: 40°C, Degree of Super Cooling: 0°C)

R134a/ cyclopentane molar ratio	100/0	80/20	70/30	50/50	20/80	10/90	0/100
Performance Coefficient (-)	3.07	3.12	3.57	3.89	4.10	4.07	3.59
Refrigeration Capacity ($kcal/m^3$)	210	55	35	25	20	15	10

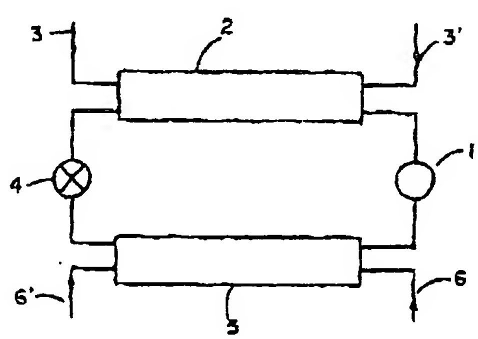
[Advantageous Effect of the Invention]

The working medium mixtures of this invention show particularly excellent refrigeration cycle efficiency, that is, refrigeration and heating efficiencies, and substantial improvement over tetrafluoroethane.

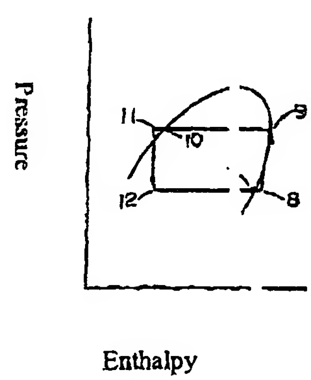
[Brief Explanation of the Figures]

Figure 1 is a refrigeration cycle for illustrating an example of this invention; Figures 2 and 3 are filled-in pressure-enthalpy diagrams for cycles when the working medium mixtures of the present invention are used as working media.

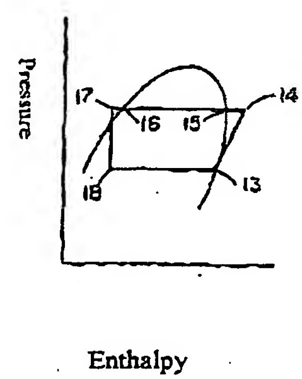
[Figure 1]



[Figure 2]



[Figure 3]



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